Selective dehydroisomerization of cyclic monoterpenes to p-cymene over silica-supported CdO

Aliyah Alsharif [a,b], Elena F. Kozhevnikova [a], Ivan V. Kozhevnikov [a,*]

[a] Department of Chemistry, University of Liverpool, Liverpool L69 7ZD, United Kingdom
[b] Department of Chemistry, Faculty of Science, Al-Imam Muhammad Ibn Saud University, Riyadh, Saudi Arabia

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ABSTRACT

Cadmium oxide supported on silica is a highly active and selective bifunctional catalyst for the clean synthesis of p-cymene using dehydroisomerization of cyclic monoterpenes such as α-pinene, β-pinene, limonene, α-terpinene, γ-terpinene, and terpinolene. The dehydroisomerization occurs via acid-redox bifunctional catalysis at the gas-solid interface involving isomerization of monoterpenes to p-menthadienes on acid sites of silica support followed by p-menthadiene dehydrogenation to p-cymene on oxo-metal sites of CdO. The less reactive bicyclic monoterpenes, such as α-pinene and β-pinene, give 91–95% p-cymene yields at 325–375 °C, whereas more reactive monocyclic monoterpenes, such as limonene, α-terpinene, γ-terpinene, and terpinolene, give a 100% yield at 200–250 °C. To the best of our knowledge, CdO/SiO$_2$ has the highest efficiency in monoterpene-to-p-cymene dehydroisomerization among the catalysts reported so far. The catalyst was characterized by BET, TGA, XRD, DRIFTS, H$_2$-TPR, and ICP–OES.

1. Introduction

Catalytic conversion of renewable terpene feedstocks into value-added chemicals has long been an area of considerable interest [1–5]. In the past two decades, it has become one of the priority directions for sustainable development [6–17]. In this context, our work is concerned with the development of new, more efficient catalysts for sustainable synthesis of p-cymene, which has many uses, from medical and cosmetic products to manufacturing commodity chemicals [17]. The major application of p-cymene is for the synthesis of p-cresol, an intermediate in the manufacturing of antioxidants [18]. Selective oxidation of the bio-derived p-cymene is contemplated as a sustainable route to terephthalic acid ([14–16] and references therein). Traditionally, p-cymene is produced from petroleum-based feedstocks by the Friedel-Crafts alkylation of toluene by propene [17], with an adverse effect on the environment. An alternative environment-friendly route to p-cymene utilizes dehydroisomerization of renewable monoterpene feedstocks, such as α-pinene and limonene, using bifunctional heterogeneous catalysis [17]. These monoterpenes are obtained from abundantly available low-cost resources such as turpentine oils, crude sulfate turpentine, and citrus fruits [17,19,20].

The dehydroisomerization of α-pinene to p-cymene occurs over acid-redox bifunctional catalysts at the gas-solid interface at 300–460 °C and atmospheric pressure. First, α-pinene is isomerized on acid sites to form monocyclic p-menthadienes together with bicyclic and tricyclic terpenes; this follows by p-menthadiene dehydrogenation on metal or oxo-metal sites [17] (Scheme 1). It is suggested that the isomerization proceeds through protonation of the C=C bond of α-pinene to generate pinanyl cation. The latter rearranges to bicyclic and tricyclic terpenes, such as camphene, β-pinene, and tricyclene, and to monocyclic terpenes (p-menthadienes), such as limonene, terpinolene, terpinene, etc. (Scheme 1) [17]. The formation of bicyclic and tricyclic terpenes is favored at lower temperatures, while p-menthadienes appear at higher temperatures [17]. In the dehydroisomerization of α-pinene to p-cymene, p-menthadiene dehydrogenation is likely to be the rate-limiting step, with the isomerization step probably being at quasi-equilibrium [17]. Many heterogeneous catalysts have been disclosed for α-pinene dehydroisomerization [17,21–25]. Among them are Cr$_2$O$_3$/Al$_2$O$_3$ (390–460 °C, 53% p-cymene yield) [22], zeolite Y (300 °C, 54% yield) [23], Pd/SiO$_2$ (300 °C, 67% yield) [17], Pd-Zn/Al-SBA-15 (300 °C, 77% yield) [24], and bulk Zn(II)–Cr(III) mixed oxide (350 °C, 78% yield) [25]. Pd catalysts require hydrogen supply to prevent their deactivation [17].

The dehydroisomerization of limonene to p-cymene is easier to occur

* Corresponding author.
  E-mail address: kozhev@liverpool.ac.uk (I.V. Kozhevnikov).

than the reaction of α-pinene. This is because the reaction of limonene does not involve C–C bond breaking. The dehydroisomerization of limonene to p-cymene probably proceeds via a bifunctional mechanism, which involves fast limonene isomerization on acid sites followed by slow dehydrogenation on metal or oxo-metal sites of a bifunctional catalyst [26–39] (Scheme 2). The dehydroisomerization of limonene can be carried out in the gas or liquid phase in the presence of various heterogeneous catalysts [27–39]. These include Ti/SBA-15 (liquid phase, 160 °C, 56% p-cymene yield) [28], Pd/HZSM-5 (liquid phase, 260 °C, 8 bar, 82% yield) [29], Pd/Al$_2$O$_3$ (supercritical ethanol, 300 °C, 65 bar, 80% yield) [30], TiO$_2$ (gas phase, 300 °C, 90% yield) [31], Pd/SiO$_2$ (gas phase, 300 °C, in H$_2$ flow, 99% yield) [32], and others [27]. Pd/SiO$_2$ gives the highest yield of p-cymene, however, it requires a hydrogen supply to prevent catalyst deactivation [32].

Recently, we have reported that silica-supported zinc oxide is an efficient noble-metal-free catalyst for the synthesis of p-cymene by the gas-phase dehydroisomerization of α-pinene and limonene [40]. The reaction of α-pinene over ZnO/SiO$_2$ produces p-cymene with 90% yield at 100% conversion at 370 °C. The reaction with limonene gives a 100% p-cymene yield at 325 °C. The ZnO/SiO$_2$ catalyst shows stable performance for over 70 h without co-feeding hydrogen.

Here, we report silica-supported cadmium oxide, CdO/SiO$_2$, as a new highly efficient noble-metal-free catalyst for the dehydroisomerization of monoterpenes to p-cymene in the gas phase. Cadmium is a close Group 12 analog of zinc. CdO is known as a multifunctional material for its application in optoelectronic devices ([41] and references therein). It has also been reported as a Lewis acid-base and dehydrogenation catalyst, for example, for condensation of aldehydes [41], dehydration of ethanol [42], and dehydrogenation of ethylbenzene and cycloalkanes [43]. Here, it is demonstrated that CdO/SiO$_2$ has the highest efficiency in monoterpene-to-p-cymene dehydroisomerization among the catalysts reported so far, to the best of our knowledge. A wide range of cyclic monoterpenes is studied in this work; these include not only α-pinene and limonene, which are well documented as the feedstocks for p-cymene synthesis, but also β-pinene, α-terpinene, γ-terpinene, and terpinolene. The latter are often missing from the literature but are important components of industrial turpentine feedstocks. It is demonstrated that all these monoterpenes can be converted to p-cymene with excellent yields of 91–100% using CdO/SiO$_2$ as the catalyst.

2. Experimental

Monoterpenes α-pinene (>98%), 1S-(-)-β-pinene (99%), R-(+)-limonene (>97), terpinolene (>85%), α-terpinene (85%), and γ-terpinene (>97%) were purchased from Sigma–Aldrich and used as supplied without further purification. Hereinafter, 1S-(-)-β-pinene and R-(+)-limonene are referred to as β-pinene and limonene for short. Cd(NO$_3$)$_2$·4 H$_2$O was also from Sigma–Aldrich. Aerosil 300 silica support ($S_{BET} \approx 300$ m^{2}g^{-1}) was from Degussa.

CdO/SiO$_2$ catalysts (5–30 wt% CdO loading) were prepared by wet impregnation of Aerosil 300 with Cd(NO$_3$)$_2$ from an aqueous solution. The catalysts were calcined in air at 400 or 500 °C for 2 h (5 °C min^{-1} ramp rate) to decompose Cd(II) nitrate to CdO to afford CdO/SiO$_2$ catalysts as white powders. The catalysts were crushed to 45–140 μm particle size. From ICP–OES analysis, CdO loadings were close to the expected nominal loadings within ± 1 wt%. Bulk cadmium oxide was prepared by air calcination of Cd(NO$_3$)$_2$·4 H$_2$O at 400 °C for 2 h with a temperature ramp rate of 5 °C min^{-1} to afford CdO as a black powder. Information about the catalysts prepared is given in Table 1. *Cadmium is a very toxic metal. It has a variety of toxic effects including nephrotoxicity, carcinogenicity, teratogenicity and endocrine and reproductive toxicities [44]. The preparation and handling of CdO catalysts must be carried out with great care, especially at high temperatures, using appropriate personal protective equipment.*

The characterization techniques (BET, XRD, TGA, H$_2$-TPR, ICP–OES, DRIFT spectroscopy, and GC–MS) have been described elsewhere [40]; the details are given in the Supporting Information.

The dehydroisomerization of monoterpenes was carried out at 200–400 °C and atmospheric pressure in a continuous flow fixed-bed quartz reactor with online GC analysis, as described previously [40]. The details of catalyst testing and product analysis are presented in the Supporting Information. Fig. S1 illustrates the GC analysis of products.

3. Results and discussion

3.1. Catalyst characterization

The CdO/SiO$_2$ catalysts were prepared by wet impregnation of Cd(NO$_3$)$_2$ onto Aerosil 300 silica from an aqueous solution followed by air calcination at 400 or 500 °C. Upon calcination, cadmium nitrate decomposed to form CdO on the silica surface. Bulk CdO was prepared by thermal decomposition of Cd(NO$_3$)$_2$·4 H$_2$O at 400 °C [45]. As can be seen from the TGA trace (Fig. 1), the thermal decomposition of Cd(NO$_3$)$_2$·4 H$_2$O occurs in several steps including the loss of two H$_2$O molecules at ~100 °C and the other two at 200 °C followed by the decomposition of Cd(NO$_3$)$_2$ to CdO starting at ~400 °C and finishing at 500 °C, with no weight loss upon further heating at least up to 700 °C. These results are in good agreement with the previous report [45]. The formation of bulk CdO upon Cd(NO$_3$)$_2$·4 H$_2$O decomposition at 400 °C (air calcination at 400 °C, 5 °C min^{-1}, 2 h) was confirmed by XRD (Fig. 2). The bulk CdO thus obtained was a crystalline material with a face-centered (fcc) structure and an average particle size of 156 nm. The
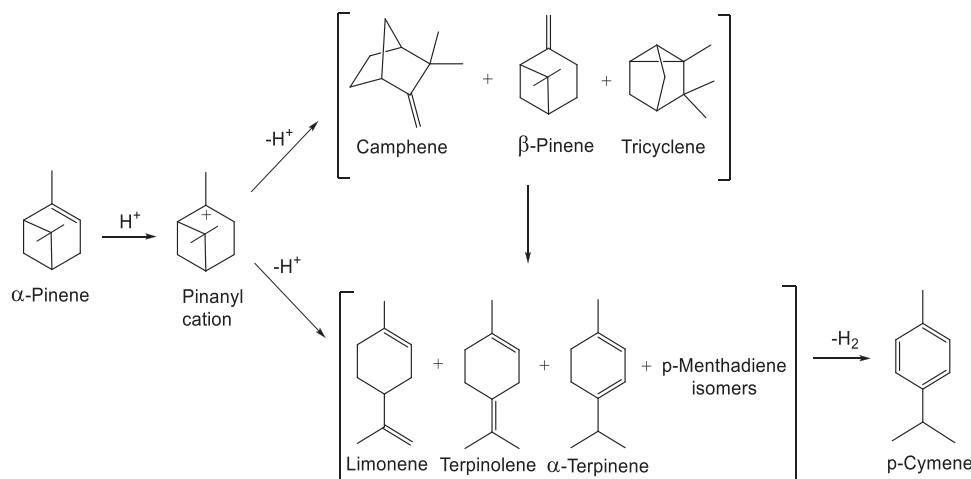
Scheme 1. Reaction network for α-pinene-to-p-cymene dehydroisomerization.
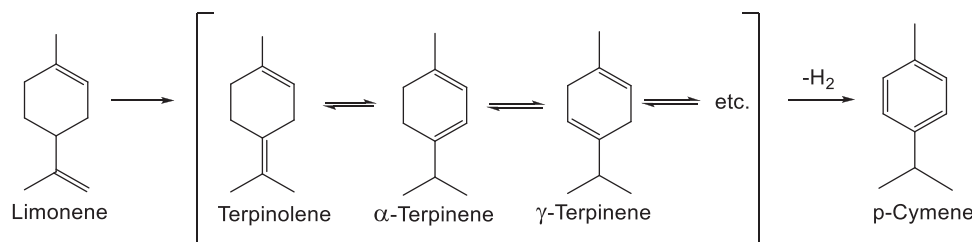
Scheme 2. Reaction pathway for limonene-to-p-cymene dehydroisomerization.

Table 1
Information about catalysts.

Catalyst[a]	S_{BET}[b] m² g⁻¹	Pore volume[c] cm³ g⁻¹	Pore size[d] Å	Weight loss[e] wt%
CdO	0.35	0.00013	15	1.0
CdO[f]	15	0.069	185	0.2
5%CdO/SiO₂	250	1.05	167	3.0
10%CdO/SiO₂	208	0.86	156	6.5
10%CdO/SiO₂[f]	230	1.04	180	4.0
20%CdO/SiO₂	172	0.89	207	6.6
30%CdO/SiO₂	126	0.74	235	4.2

[a] Catalysts calcined in air at 400 °C unless stated otherwise.
[b] BET surface area.
[c] Single point total pore volume.
[d] Average pore diameter by BET method.
[e] From TGA in the temperature range of 25–700 °C.
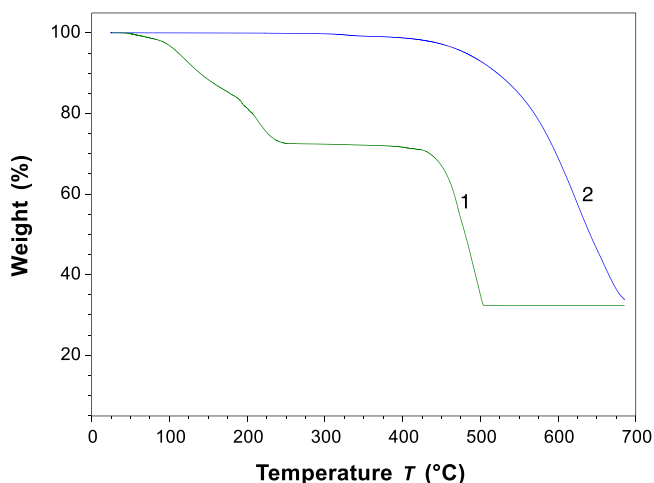[f] Catalysts calcined in air at 500 °C.

Fig. 1. TGA of Cd(NO₃)₂·4 H₂O in air flow, 10 °C min⁻¹ (1); and TGA of CdO calcined at 500 °C, in H₂–N₂ (5:95) flow, 20 °C min⁻¹ (2).

XRD pattern of CdO is in perfect agreement with the literature data (JCPDS card no. 65–2908), with reflections at 33.0° (111), 38.3° (200), 55.3° (220), 65.9° (311), and 69.3° (222). No characteristic peaks for any impurities were detected, confirming that the CdO obtained was phase pure. CdO sample obtained by air calcination at 500 °C/2 h had the same XRD pattern. In contrast to the crystalline bulk CdO, the CdO/SiO₂ catalysts were all amorphous (Fig. 2). Therefore, the XRD data indicates that cadmium oxide had a fine dispersion on the surface of silica.

From the BET analysis, CdO/SiO₂ catalysts exhibited adsorption/desorption isotherms characteristic of mesoporous materials with an H1
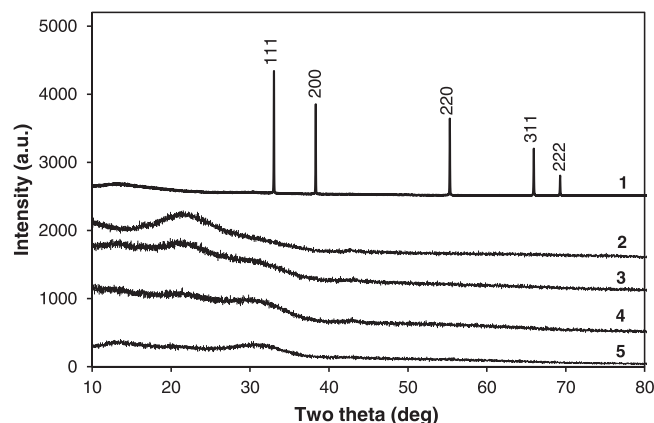

Fig. 2. Powder XRD (CuKα) for bulk CdO (1), 5%CdO/SiO₂ (2), 10%CdO/SiO₂ (3), 20%CdO/SiO₂ (4) and 30%CdO/SiO₂ (5); all catalysts calcined at 400 °C.

hysteresis loop typical of amorphous silica (Fig. S2). Bulk CdO prepared by calcining Cd(NO₃)₂·4 H₂O at 400 °C had a low surface area of 0.35 m²g⁻¹ and a tiny pore volume. Both the surface area and pore volume of CdO increased after calcination at 500 °C to 15 m²g⁻¹ and 0.069 cm³g⁻¹, respectively. As expected, supported CdO/SiO₂ catalysts had a much larger total surface area; the surface area and pore volume decreased with increasing CdO loading. Similar to the bulk CdO, the surface area and porosity of CdO/SiO₂ increased with increasing the calcination temperature from 400 to 500 °C (see the data for 10%CdO/SiO₂ in Table 1).

H₂-TPR was performed on fresh 10%CdO/SiO₂ calcined at 500 °C to assess the possibility of CdO reduction during terpene dehydroisomerization, which, along with p-cymene, produced hydrogen (less than 0.5% in the gas flow at 200–400 °C under our reaction conditions). As seen from the H₂-TPR trace (Fig. 3), CdO in this catalyst was reduced to Cd metal at 477 °C (see the details in the Supporting Information). Additionally, TGA of bulk CdO calcined at 500 °C was performed under a
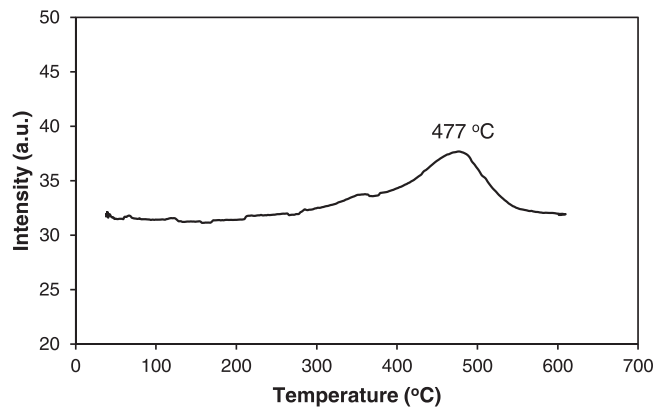

Fig. 3. H₂-TPR of 10%CdO/SiO₂ (40 mg) calcined at 500 °C in H₂–N₂ (5:95) flow (40 ml min⁻¹), 20 °C min⁻¹.

mixed H_2–N_2 (5:95) flow (Fig. 1). The TGA shows that CdO was reduced to metal above 450 °C; the Cd metal formed (m.p. 321 °C) evaporated, with a 66% weight loss to 700 °C (only a 12% weight loss expected if CdO reduced without Cd metal evaporation). These results rule out CdO reduction during the dehydroisomerization reaction as in most cases it was carried out at 200–325 °C, with less than 0.5% H_2 produced in the gas stream.

From the DRIFT spectroscopy of adsorbed pyridine, CdO/SiO$_2$ catalysts exhibited a strong band at 1450 cm^{-1} (Fig. 4) indicating the presence of Lewis acid sites [46]. The band at 1540 cm^{-1} characteristic of Brønsted acid sites [46] was hardly seen at all. We were unable to obtain good DRIFT spectra for pyridine adsorbed on bulk CdO due to its very low surface area (Table 1). DRIFT spectrum for anhydrous Cd (NO$_3$)$_2$, prepared by calcining Cd(NO$_3$)$_2$·4 H$_2$O at 300 °C displays only Lewis acid sites (Fig. 4). These results show that the CdO catalysts possess Lewis acidity, lacking Brønsted acid sites capable of protonating pyridine.

From TGA, the CdO/SiO$_2$ catalysts exhibited a weight loss of 3.0–6.6% upon heating from 25 to 700 °C (Table 1, Fig. S3), which can be attributed to the loss of physisorbed and chemically bound water. About half of this water was lost above 100 °C, which points to the existence of silanol groups in the catalysts. This is also supported by DRIFT spectroscopy. Fig. 5 presents the DRIFT spectra of Aerosil 300 silica and CdO/SiO$_2$ catalysts in the region of the OH stretch of silanol groups. These spectra are similar to those for ZnO/SiO$_2$ catalysts reported previously [40]. In the DRIFT spectrum of the neat silica, the strong band at 3744 cm^{-1} is assigned to the free terminal silanol groups. The bands at 3600–3700 cm^{-1} are attributed to the hydrogen-bonded vicinal silanols. The broad band at 3100–3600 cm^{-1} is assigned to silanol nests; the latter include different silanol groups linked by extended hydrogen bonding [47–49]. In CdO/SiO$_2$ catalysts, the free terminal silanol groups and silanol nests are present, whereas the hydrogen-bonded vicinal silanols are less visible, similar to ZnO/SiO$_2$ catalysts reported previously [40]. Despite being weak Brønsted acid sites, the silanol groups can readily isomerize α-pinene and limonene at 300 °C [17,32].

3.2. Dehydroisomerization of α-pinene

Table 2 shows the results of the initial testing of CdO/SiO$_2$ catalysts calcined at 400 °C in α-pinene dehydroisomerization (250 °C, weight hourly space velocity WHSV = 0.08 h^{-1}, 4 h time on stream (TOS)). At such conditions, CdO/SiO$_2$ catalysts exhibited high activity, with p-cymene selectivity of 70–75%. α-Pinene conversion reached > 98% within 1 h TOS and further increased to 100% (Fig. 6). The formation of hydrogen in the reaction was confirmed by GC-TCD (see GC trace in
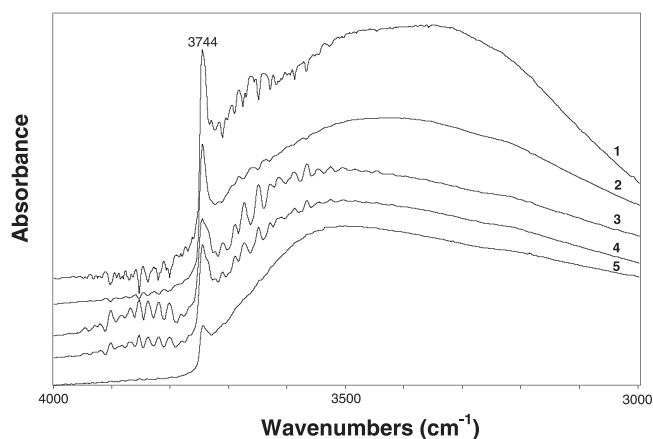

Fig. 5. DRIFT spectra of SiO$_2$ (1), 5%CdO/SiO$_2$ (2), 10%CdO/SiO$_2$ (3), 20% CdO/SiO$_2$ (4), and 30%CdO/SiO$_2$ (5) calcined at 400 °C (powdered KBr mixtures versus KBr).

Fig. S4). CdO loading in the range of 5–30 wt% had a small effect on catalyst performance. Nevertheless, 10%CdO/SiO$_2$ exhibited a better performance among these catalysts, giving 75% p-cymene selectivity at 100% conversion. As can be seen from Fig. 6, this catalyst gave stable p-cymene selectivity for over 4 h TOS. There was an initial increase in α-pinene conversion before reaching a steady state (Fig. 6); this may be due to catalyst coking which could provide extra adsorption sites for α-pinene and hence enhance its conversion. 10%CdO/SiO$_2$ calcined at 500 °C gave a higher p-cymene selectivity, 77%, compared to the catalyst calcined at 400 °C (Table 2). Although the difference in selectivity is within experimental error ($\leq$ 5%), this trend was observed at different contact times, with a 2–3% difference in p-cymene selectivity (Fig. S5), hence appearing statistically significant. The better performance of 10%CdO/SiO$_2$ calcined at 500 °C can be attributed to a structural change of CdO on the silica surface. As seen from the data in Table 1, the texture of bulk CdO changed greatly upon increasing the calcination temperature from 400 to 500 °C, thus indicating a significant structural change.

Bulk CdO hardly showed any activity at all (Table 2), which can be attributed to its very low surface area (Table 1) as well as to the lack of Brønsted acidity (see above). Pure silica support in the absence of CdO showed high isomerization activity (97% α-pinene conversion, Table 2), mainly producing limonene, camphene, and other p-menthadiene isomers (referred to as "other") together with some cracking products (referred to as "lights"). Notably, no formation of p-cymene was observed on pure SiO$_2$, which is not unexpected because silica lacks the dehydrogenation function. p-Cymene was formed only in the presence of CdO, which is known to possess the dehydrogenation function [43]. These results are consistent with the mechanism [17,40] involving a fast step of α-pinene isomerization to p-menthadienes on acid sites (silanol groups of silica) followed by a slow step of dehydrogenation of p-menthadienes to p-cymene on oxo-metal sites of cadmium oxide (Scheme 1).

Fig. S6 shows a long-term test (25 h TOS) for α-pinene dehydroisomerization over 10%CdO/SiO$_2$ calcined at 500 °C. After 25 h on stream at 250 °C and WHSV = 0.013 h^{-1}, the selectivity to p-cymene only slightly reduced from 78% to 74%. This could be attributed to catalyst coking. After the reaction, the initially white 10%CdO/SiO$_2$ catalyst became grey; 0.5% of carbon deposition was found in the post-reaction catalyst by combustion elemental analysis. The catalyst could be regenerated in situ by the air flow at 400 °C for 3 h, which reduced coke deposition to 0.1% and restored catalyst activity (Fig. S7). XRD analysis of spent 10–30% CdO/SiO$_2$ catalysts after α-pinene dehydroisomerization (250 °C, WHSV = 0.08 h^{-1}, 4 h TOS) is shown in Fig. S8. The spent catalysts are amorphous; their diffractograms are similar to those for the corresponding fresh catalysts (Fig. 2). No
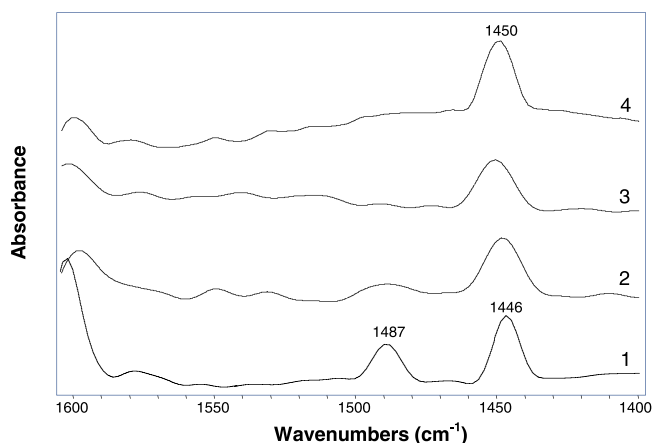

Fig. 4. DRIFT spectra of adsorbed pyridine (powdered KBr mixtures versus KBr): anhydrous Cd(NO$_3$)$_2$ calcined at 300 °C (1), Aerosil 300 silica (2), 5% CdO/SiO$_2$ (3), and 10%CdO/SiO$_2$ (4).

Table 2
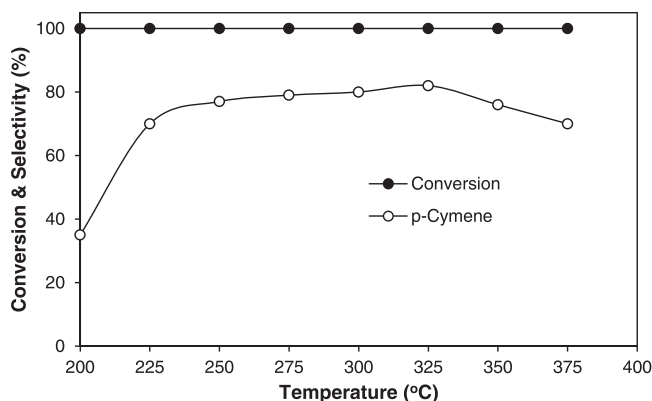Dehydroisomerization of α-pinene to p-cymene over CdO/SiO$_2$.[a]

Catalyst	Conversion %[b]	Selectivity %mol[b]				
		Lights	Camphene	Limonene	p-Cymene	Other
SiO$_2$	97	25	21	16	0	38
CdO[c]	1	0	0	0	0	1
5%CdO/SiO$_2$[c]	100	8	15	0	75	2
10%CdO/SiO$_2$[c]	100	8	15	0	75	2
10%CdO/SiO$_2$[d]	100	9	13	0	77	1
20%CdO/SiO$_2$[c]	100	9	17	0	73	1
30%CdO/SiO$_2$[c]	100	9	19	0	70	2

[a] 0.20 g catalyst, 250 °C, 0.48 kPa α-pinene partial pressure, 10 ml min^{-1} flow rate, 4 h TOS, WHSV = 0.08 h^{-1}.
[b] Average conversion and product selectivity within 1–4 h TOS.
[c] The catalysts calcined at 400 °C.
[d] 10%CdO/SiO$_2$ calcined at 500 °C.
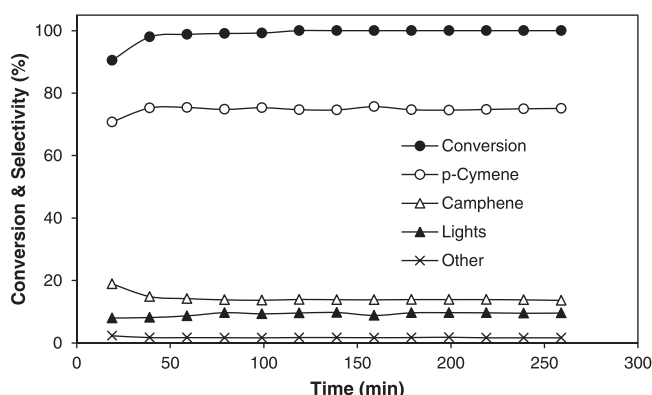
Fig. 6. Time course for α-pinene dehydroisomerization over 10%CdO/SiO$_2$ calcined at 400 °C: 0.20 g catalyst, 250 °C, 0.48 kPa α-pinene partial pressure, 10 ml min^{-1} flow rate, WHSV = 0.08 h^{-1}.

reflections of Cd metal phase (JCPDS 03–065–3363) can be seen in these diffractograms.

Fig. 7 shows the effect of reaction temperature on p-cymene selectivity in the presence of 10%CdO/SiO$_2$ calcined at 500 °C; the temperature was varied from 200 to 375 °C at WHSV = 0.08 h^{-1}. The conversion of α-pinene was 100% within this temperature range. The selectivity to p-cymene increases with the temperature reaching 82% at 325 °C and then declines as the temperature is further increased. The latter can be explained by catalyst coking.

Fig. 8 shows the effect of contact time, (WHSV)$^{-1}$, on p-cymene selectivity at the optimum temperature of 325 °C in the presence of 10%

Fig. 7. Effect of temperature on α-pinene dehydroisomerization over 10%CdO/SiO$_2$ calcined at 500 °C: 0.20 g catalyst, 0.48 kPa α-pinene partial pressure, 10 ml min^{-1} flow rate, WHSV = 0.08 h^{-1}.
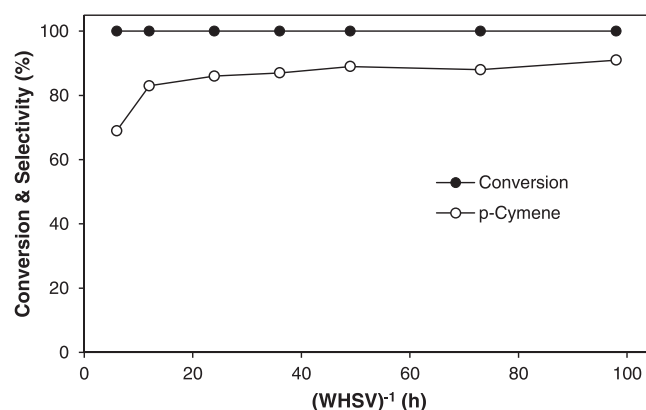
Fig. 8. α-Pinene conversion and p-cymene selectivity for 10%CdO/SiO$_2$ calcined at 500 °C at different contact times (325 °C, 0.48 kPa α-pinene partial pressure, 4 h TOS); the contact time varied by changing flow rate (5–20 ml min^{-1}) and catalyst amount (0.2–0.8 g).

CdO/SiO$_2$ calcined at 500 °C. The contact time was varied by changing the flow rate from 5 to 20 ml min^{-1} and the amount of catalyst from 0.2 to 0.8 g. Under such conditions, α-pinene conversion was 100%. The results show that the selectivity increases steadily with the contact time, as expected for a consecutive reaction (Scheme 1), reaching 91% (91% p-cymene yield) at a contact time of 100 h (WHSV = 0.01 h^{-1}). From these results, the CdO/SiO$_2$ catalyst outperforms the ZnO/SiO$_2$ catalyst reported previously [40]; the latter provides 90% p-cymene yield at the same WHSV but at a significantly higher reaction temperature of 370 °C.

3.3. Dehydroisomerization of β-pinene

Dehydroisomerization of β-pinene is less well studied as compared to α-pinene. The two pinene isomers have similar structures differing only in the position of the C=C double bond. The dehydroisomerization of β-pinene is likely to occur via a mechanism similar to that for the reaction of α-pinene, involving the isomerization of β-pinene to p-menthadienes through pinanyl cation intermediate followed by dehydrogenation to form p-cymene (Scheme 3).

The dehydroisomerization of β-pinene was studied in the presence of 10%CdO/SiO$_2$ catalyst calcined at 500 °C, which showed the best performance in the reaction of α-pinene (see above). Table 3 shows representative results at different reaction temperatures 200–400 °C. The data for the reaction with 20%CdO/SiO$_2$ calcined at 400 °C is also included for comparison with other monoterpenes studied (see Section 3.6 below). As seen, in the whole temperature range, β-pinene conversion on 10%CdO/SiO$_2$ was 99–100%. The reaction had stable product selectivity for over 4 h TOS (Fig. 9). The selectivity to p-cymene increases with increasing reaction temperature reaching a maximum of
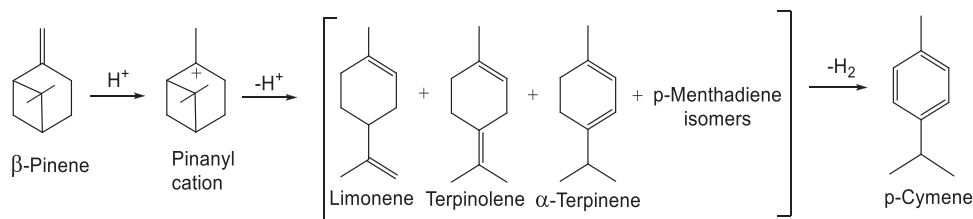
**Scheme 3.** Dehydroisomerization of β-pinene to p-cymene.

Table 3

Effect of temperature on β-pinene dehydroisomerization over 10%CdO/SiO₂.[a]

Temp.°C	Conv.[b] %	Selectivity %mol[b]						
		Lights	α-Pinene	Camphene	α-Terpinene	ρ-Cymene	γ-Terpinene	Terpinolene
200	99	6	1	24	10	52	3	4
225	100	5	1	20	6	63	2	3
250	100	7	0	14	1	78	0	0
250[c]	100	8	2	22	3	66	0	0
275	100	8	0	12	0	80	0	0
300	100	9	0	9	0	82	0	0
325	100	9	0	8	0	83	0	0
350	100	8	0	7	0	85	0	0
375	100	8	0	4	0	88	0	0
400	100	9	0	4	0	86	1	0

[a] 0.20 g 10%CdO/SiO₂ catalyst calcined at 500 °C, 0.47 kPa β-pinene partial pressure, 10 ml min⁻¹ flow rate, WHSV = 0.08 h⁻¹.
[a] $0.20\ \text{g}\ 10\%\text{CdO/SiO}_2$ catalyst calcined at 500 °C, 0.47 kPa β-pinene partial pressure, 10 ml min^{-1} flow rate, WHSV $= 0.08\ \text{h}^{-1}$.
[b] Average conversion and product selectivity within 1–4 h TOS.
[c] 20%CdO/SiO₂ catalyst calcined at 400 °C.
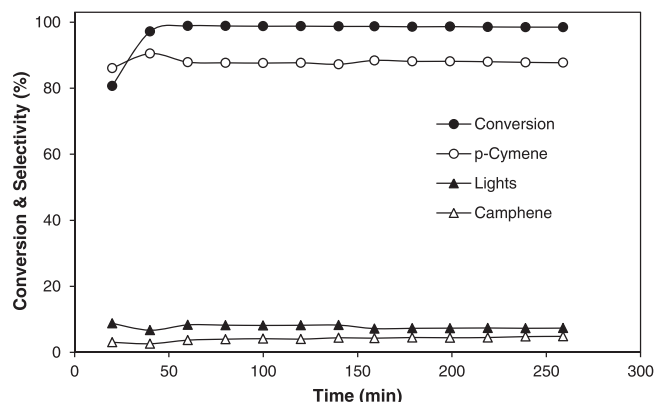
Fig. 9. Time course for β-pinene dehydroisomerization over 10%CdO/SiO₂ calcined at 500 °C: 0.20 g catalyst, 375 °C, 0.47 kPa β-pinene partial pressure, 10 ml min^{-1} flow rate, WHSV $= 0.08\ \text{h}^{-1}$.

Fig. 10. Effect of temperature on β-pinene dehydroisomerization over 10% CdO/SiO₂ calcined at 500 °C: 0.20 g catalyst, 0.47 kPa α-pinene partial pressure, 10 ml min^{-1} flow rate, WHSV $= 0.08\ \text{h}^{-1}$.

88% at 375 °C and then declines at higher temperatures. Fig. 10 displays the effect of temperature on p-cymene selectivity in more detail, with the maximum selectivity at 375 °C. The main by-products were camphene and lights; the amount of camphene decreased whereas the amount of the lights increased with increasing temperature (Table 3).

The selectivity to p-cymene was found to increase with increasing the contact time, (WHSV)$^{-1}$ (Fig. 11), similar to the reaction of α-pinene. The contact time was varied at the optimum temperature of 375 °C by changing the flow rate from 5 to 20 ml min^{-1}, the catalyst amount from 0.2 to 0.8 g, and the β-pinene partial pressure from 0.36 to 0.66 kPa. As can be seen, p-cymene selectivity levels off at contact times > 40 h, reaching 95% at 100% β-pinene conversion. Therefore, the dehydroisomerization of β-pinene over CdO/SiO₂ gives 95% p-cymene yield at 375 °C and WHSV = 0.02 h^{-1}, which is higher than the p-cymene yield obtained from α-pinene (91% at 325 °C), although achieved at a higher temperature.
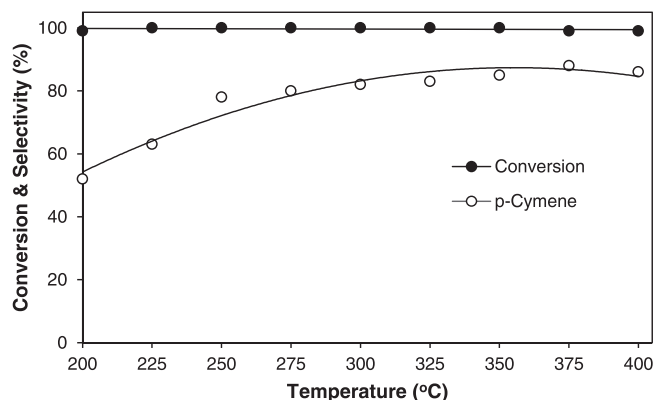
3.4. Dehydroisomerization of limonene

Dehydroisomerization of limonene to p-cymene occurs easier than that of α-pinene because it does not involve C–C bond breaking during the reaction (Scheme 2) and generally gives a higher p-cymene yield compared to the reaction of α-pinene [17,32,40]. In the limonene dehydroisomerization, CdO/SiO₂ calcined at 400 °C was found to be a highly efficient catalyst, providing 100% p-cymene yield at 250 °C.

Table 4 shows the effect of CdO loading (10–30%) on limonene conversion and p-cymene selectivity for the reaction at two temperatures of 225 and 250 °C and a space velocity WHSV = 0.08 h^{-1}. It can be seen that under such conditions the reaction occurs with 97–100% limonene conversion and 97–100% p-cymene selectivity. β-Pinene was the only byproduct observed in this reaction. The loading of CdO had a small effect on the performance of CdO/SiO₂ catalysts. Among these catalysts, 20%CdO/SiO₂ and 30%CdO/SiO₂ exhibited a higher efficiency, providing 100% selectivity to p-cymene at 100% limonene
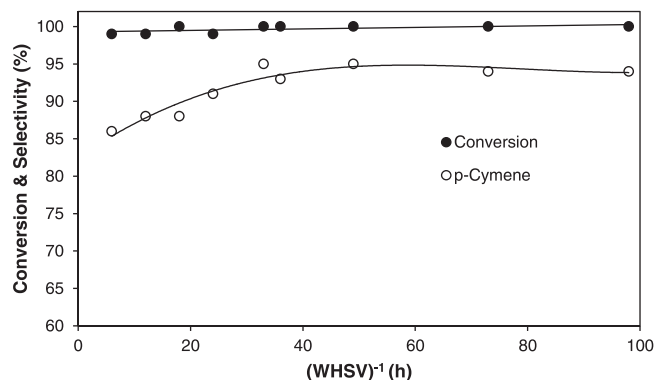
Fig. 11. Plot of β-pinene conversion and p-cymene selectivity over 10%CdO/SiO₂ calcined at 500 °C versus contact time at 375 °C; the contact time varied by changing flow rate (5–20 ml min⁻¹), catalyst amount (0.2–0.8 g) and β-pinene partial pressure (0.36–0.66 kPa).

Table 4
Dehydroisomerization of limonene to p-cymene over CdO/SiO₂.[a]

| Catalyst[b]	Temperature	Conversion[c] %	Selectivity %mol[c]	
	°C		β-Pinene	p-Cymene
10%CdO/SiO₂	225	98	3	97
10%CdO/SiO₂	250	100	1	99
20%CdO/SiO₂	225	100	2	98
20%CdO/SiO₂	250	100	0	100
30%CdO/SiO₂	225	97	2	98
30%CdO/SiO₂	250	100	0	100

[a] 0.20 g catalyst, 10 ml min⁻¹ flow rate, 0.47 kPa limonene partial pressure, WHSV = 0.08 h⁻¹, 4 h TOS.
[b] The catalysts calcined at 400 °C.
[c] Average conversion and product selectivity over 1–4 h TOS.

conversion (100% p-cymene yield) at 250 °C. This differs from the reaction of α-pinene and β-pinene, where the optimal CdO loading was 10 wt% (Table 2). This result can be attributed to the lower temperature for the reaction of limonene (250 °C) as compared to the reactions of α-pinene and β-pinene (325–375 °C). The lower reaction temperature necessitates a higher loading of the dehydrogenation component, cadmium oxide, for the limonene-to-p-cymene dehydroisomerization. Similar results have been reported for ZnO/SiO₂ catalyst [40].

Fig. 12 shows the effect of temperature on the performance of 20% CdO/SiO₂ and 30%CdO/SiO₂ in the temperature range of 200–300 °C at WHSV = 0.08 h⁻¹. For both catalysts, the selectivity to p-cymene steadily grows with increasing the temperature to reach 100% at 250 °C,
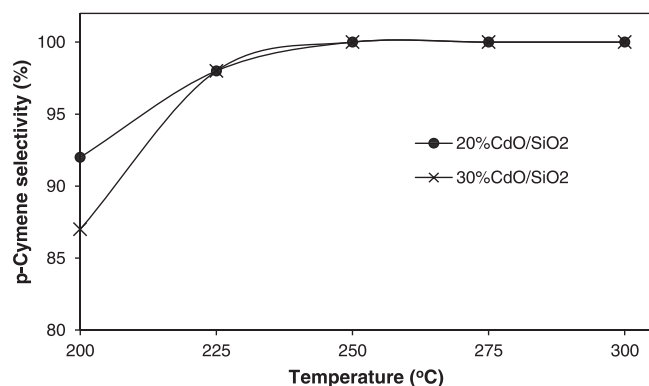
Fig. 12. Effect of temperature on limonene dehydroisomerization over 20% CdO/SiO₂ and 30%CdO/SiO₂: 0.20 g catalyst, 0.47 kPa limonene partial pressure, 10 ml min⁻¹ flow rate, 4 h TOS, WHSV = 0.08 h⁻¹; 100% limonene conversion in all cases.

with limonene conversion being 100% within the entire temperature range. This confirms that the optimum temperature for the limonene-to-p-cymene conversion is 250 °C. These results are fully consistent with the view that the dehydroisomerization of limonene occurs through the rate-limiting step of p-menthadiene dehydrogenation (Scheme 2).

The contact time was optimized for 20%CdO/SiO₂ catalyst; these results are presented in Figs. S9 and S10 in the Supporting Information. The p-cymene yield increased with increasing the contact time, (WHSV)⁻¹, to reach 100% at contact times ≥ 12 h corresponding to WHSV ≤ 0.08 h⁻¹. At optimum conditions (250 °C, WHSV = 0.08 h⁻¹), the 20%CdO/SiO₂ catalyst exhibited very stable performance for 24 h TOS (Fig. S11). Limonene conversion only slightly reduced from 100% to 97% in 24 h TOS, with an average conversion and p-cymene selectivity being 99.1% and 99.2%, respectively.

Finally, in limonene dehydroisomerization, 20%CdO/SiO₂ catalyst outperforms ZnO/SiO₂ catalyst reported previously [40]. ZnO/SiO₂ provides 100% p-cymene yield at 325 °C and WHSV = 0.08 h⁻¹, whereas CdO/SiO₂ gives 100% yield at the same WHSV but at a significantly lower reaction temperature of 250 °C.

3.5. Dehydroisomerization of α-terpinene, γ-terpinene, and terpinolene

There is little data on the dehydroisomerization of the above monoterpenes in the literature. Since their framework is the same as that of limonene, differing only in the position of C═C double bonds, they can be expected to undergo an easy dehydroisomerization similar to limonene (Scheme 2).

The dehydroisomerization of α-terpinene, γ-terpinene, and terpinolene was studied using 20%CdO/SiO₂ catalyst calcined at 400 °C, which gave the best performance in the reaction of limonene (see above). Table 5 shows the results for these substrates at 250 °C and WHSV = 0.08 h⁻¹. The results for limonene are also included for comparison. As expected, all these monoterpenes exhibit similar dehydrogenation activities with 99–100% p-cymene yield under such conditions. The time courses for α-terpinene, γ-terpinene, and terpinolene are shown in Figs. S12–S14, respectively. In all cases, an average monoterpene conversion is 100% within 1–4 h TOS, with a stable p-cymene selectivity at ≥ 99% for at least 4 h TOS. β-Pinene was the only by-product observed (≤1%).

Fig. 13 shows the effect of reaction temperature on p-cymene yield in dehydroisomerization of α-terpinene, γ-terpinene, and terpinolene in the temperature range of 175–400 °C at a space velocity WHSV = 0.08 h⁻¹. It can be seen that α-terpinene and γ-terpinene reach 100% yield already at 200 °C, whereas for terpinolene this yield is reached at 275 °C and remains at this level at least up to 400 °C. However, at a longer contact time, WHSV = 0.04 h⁻¹, terpinolene gives a 100% p-cymene yield at a lower temperature of 250 °C (Fig. S15).

Therefore, not only α-pinene and limonene, which are well documented as the feedstocks for p-cymene synthesis, but also β-pinene, α-terpinene, γ-terpinene, and terpinolene that are important components of industrial turpentine feedstocks can be converted to p-cymene with excellent yields using CdO/SiO₂ as the catalyst.

Table 5
Dehydroisomerization of monoterpenes to p-cymene over 20%CdO/SiO₂.[a]

Monoterpene	Conversion %[b]	Selectivity %mol[b]	
		β-Pinene	p-Cymene
Limonene	100	0	100
α-Terpinene	100	0	100
γ-Terpinene	100	0	100
Terpinolene	100	1	99

[a] 0.20 g 20%CdO/SiO₂ catalyst calcined at 400 °C, 250 °C reaction temperature, 10 ml min⁻¹ flow rate, 0.47 kPa monoterpene partial pressure, WHSV = 0.08 h⁻¹, 4 h TOS.
[b] Average conversion and product selectivity over 1–4 h TOS.
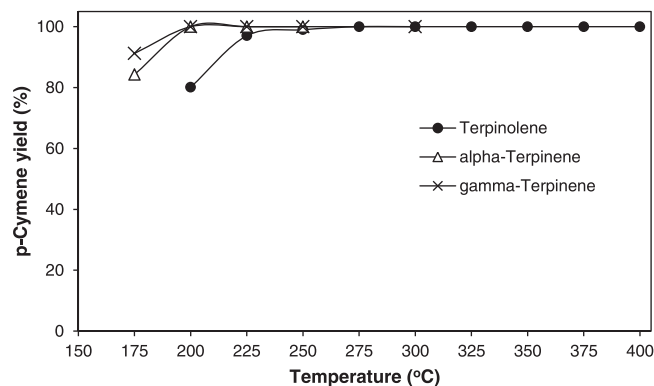
Fig. 13. Effect of temperature on p-cymene yield in monoterpene dehydroisomerization over 20%CdO/SiO$_2$ calcined at 400 °C: 0.20 g catalyst, 0.47 kPa monoterpene partial pressure, 10 ml min^{-1} flow rate, 4 h TOS, WHSV = 0.08 h^{-1}.

Industrial turpentine streams are often contaminated with sulfur compounds [17]. It has been shown that sulfur can poison Pd catalysts during crude sulfate turpentine dehydroasomerization [17]. In contrast to Pd catalysts, CdO/SiO$_2$ may be expected to be tolerant to sulfur impurities because silica-supported metal sulfides, such as ZnS, CuS, CoS, etc., have been found to perform significantly better in alkane dehydrogenation than their corresponding oxides [50]. However, the tolerance of CdO/SiO$_2$ catalysts to sulfur impurities is an open research issue.

3.6. Reaction mechanism

It is suggested that the mechanism of dehydroisomerization of monoterpenes to p-cymene on bifunctional catalysts involves two steps: fast isomerization of monoterpene reactant on Brønsted acid sites to form p-menthadiene intermediates followed by their slow dehydrogenation on metal or oxo-metal sites to p-cymene [17,25,32,40]. The mechanism of the first step is well documented in the literature. It is presented in Scheme 1. In the case of Pd/SiO$_2$ [17,32] and ZnO/SiO$_2$ [40] catalysts, this step has been shown to occur on the silanol groups of silica support possessing mild Brønsted acidity. This is also the case for the CdO/SiO$_2$ catalyst, as demonstrated by the data in Table 2. This data shows that α-pinene isomerization to p-menthadienes proceeds in the presence of silica alone with almost 100% conversion at 250 °C, whereas CdO alone, lacking Brønsted acidity, exhibits no isomerization activity. On the other hand, silica, lacking dehydrogenation ability, is incapable to dehydrogenate p-menthadienes to p-cymene, which occurs efficiently on CdO.

A proposed mechanism for the dehydrogenation step on oxo-metal sites of CdO/SiO$_2$ catalyst is shown in Scheme 4 for the dehydrogenation of α-terpinene. The dehydrogenation is suggested to proceed through the abstraction of allylic hydrogen from the substrate by the oxo-Cd(II) site followed by the elimination of another hydrogen atom to form p-cymene π-bonded to Cd(II). Then, the elimination of the p-cymene molecule and H$_2$ closes the catalytic cycle. This mechanism is based on knowledge about the mechanism of hydrocarbon dehydrogenation on metal oxides [51].

The bicyclic monoterpenes, such as α-pinene and β-pinene, are less reactive than the monocyclic ones, such as limonene, α-terpinene, γ-terpinene, and terpinolene, since the latter do not require C–C bond breaking to form p-cymene. The bicyclic monoterpenes give 91–95% p-cymene yields at 325–375 °C, whereas the monocyclic ones give a 100% yield at 200–250 °C. The monoterpenes can be ranked more accurately in their reactivity by comparing p-cymene selectivity at 100% conversion under the same reaction conditions (250 °C, 20%CdO/SiO$_2$, WHSV = 0.08 h^{-1}): β-pinene (66%) < α-pinene (73%) < terpinolene (99%) ≤ limonene, α-terpinene, γ-terpinene (100%). The importance of these
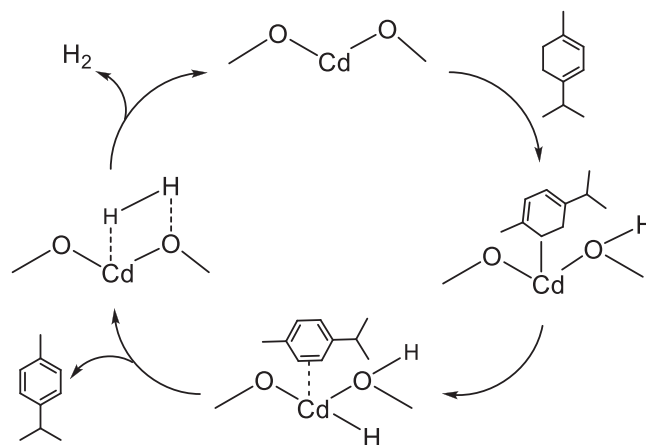
Scheme 4. Proposed mechanism of monoterpene dehydrogenation on oxo-metal sites of CdO/SiO$_2$ catalyst.

results is twofold: (i) all these monoterpenes give p-cymene with excellent yields on CdO/SiO$_2$; and (ii) the results support the bifunctional reaction mechanism. It should be noted that ranking the reactivity of monoterpenes by measuring differential rates or conversions is not possible because monoterpene conversion is determined by the fast isomerization step (~100% above 200 °C), and practically no p-cymene is formed at low conversions.

4. Conclusions

In summary, CdO/SiO$_2$ is a new highly efficient noble-metal-free catalyst for the green synthesis of p-cymene by the dehydroisomerization of cyclic monoterpenes (α-pinene, β-pinene, limonene, α-terpinene, γ-terpinene, and terpinolene). In the α-pinene-to-p-cymene reaction, this catalyst provides 91% p-cymene yield at 100% α-pinene conversion at 325 °C and WHSV = 0.01 h^{-1}. The CdO/SiO$_2$ catalyst surpasses Pd/SiO$_2$ [17], Pd-Zn/Al-SBA-15 [24], bulk Zn(II)–Cr(III) mixed oxide [25], and ZnO/SiO$_2$ [40], which provide either lower p-cymene yields (Pd catalysts) or operate at a higher temperature (ZnO/SiO$_2$ at 370 °C) or both (Zn-Cr oxide). Moreover, the Pd catalysts require continuous hydrogen supply to prevent catalyst deactivation [17,24]. The noble-metal-free CdO/SiO$_2$ catalyst does not require any hydrogen supply and it can be regenerated by air. The dehydroisomerization of β-pinene over CdO/-SiO$_2$ gives 95% p-cymene yield at 375 °C and WHSV = 0.02 h^{-1}, which is higher than the p-cymene yield obtained from α-pinene, although achieved at a higher temperature. The dehydroisomerization of limonene is much more feasible than that of α-pinene and β-pinene. The CdO/SiO$_2$ catalyst outperforms the best catalysts for the gas-phase limonene-to-p-cymene dehydroisomerization reported so far. Thus, Pd/SiO$_2$ provides a 99% yield of p-cymene at 300 °C and requires hydrogen supply to prevent catalyst deactivation [32]. ZnO/SiO$_2$ catalyst gives 100% p-cymene yield at 325 °C and WHSV = 0.08 h^{-1}. In contrast, the 20%CdO/SiO$_2$ catalyst gives 100% p-cymene yield at 250 °C and the same space velocity. α-Terpinene, γ-terpinene, and terpinolene readily undergo dehydroisomerization over CdO/SiO$_2$ similar to limonene with 100% p-cymene yield at 200–250 °C and WHSV = 0.04–0.08 h^{-1}. The most abundant monoterpenes, such as α-pinene and limonene, and industrial waste turpentine streams, such as the crude sulfate turpentine, containing a mixture of common p-menthadienes, are the renewable feedstocks for the sustainable production of p-cymene. The new CdO/SiO$_2$ catalyst is promising for the sustainable synthesis of p-cymene from renewable terpene feedstocks.

CRediT authorship contribution statement

Aliyah Alsharif: Investigation, Writing – original draft. **Elena F.**

Kozhevnikova: Supervision, Methodology. **Ivan V. Kozhevnikov:** Conceptualization, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

Acknowledgments

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.apcatb.2023.122362.

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